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Supramolecular zinc(II)salphen motifs: Reversible dimerization and templated dimeric structures

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Dedicated to Professor Gerard van Koten.

Abstract

The formation of a dimeric structure of a nonsymmetric Zn(II)salphen complex is reported. The X-ray molecular structure show the formation of an oxygen-bridged species (**2**). In addition to this structure, a pyridine-ligated complex and an 1:2 dabco/Zn(II)salphen supramolecular assembly (dabco = diazabicyclo[2.2.2]octane) are presented. Their coordination behavior has been studied and can be correlated with the substitution pattern of the salphen ligand and the donor-strength of the involved axial ligands. The Zn(II)salphen building blocks bind in a cooperative fashion to the dabco template, the second unit being bound 4 times more strongly.

Keywords: Zn(II)salphen dimers; Pyridine coordination; Non-covalent interactions

1. Introduction

Salen derivatives are among the most widely studied ligands in coordination chemistry [1]. Their structure is often considered as a representative model for the active site of biologically important metal-containing enzymes [2]. The salphen subseries (salphen = *N*,*N*′-phenylenesalicylidene) has been employed to create nearly planar, rigid N_2O_2 geometries around various metal ions, which can have vacant axial coordination sites [3]. Interestingly, in analogy to their porphyrin analogues [4] these planar structures can find application in supramolecular technology, where the axial coordination site provides a binding site that allows the construction of multi-component tailored materials [5]. A clear advantage of these salphen building blocks is their synthetic accessibility. The components (i.e., aldehydes and phenylenediamines) can be commercially purchased and are available in many structural variations, facilitating the generation of large series of supramolecular building blocks. In addition to the use of Zn(II)salen derivatives in the construction of novel functional assemblies, they have recently gained renewed interest as a result of their scope in a number of catalytic conversions [6]. This opens up new opportunities for the construction of catalytic functional assemblies.

We have recently reported the use of Zn(II)salphen complexes as components for the formation of supramolecular assemblies. Interestingly, the use of bis Zn(II)salphen complexes in combination with ditopic nitrogen ligands provided new supramolecular box

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assemblies that formed porous solid state materials [7]. In addition to these findings, we also formed Zn(II)salphen encapsulated phosphine assemblies that were applied in homogeneously catalyzed hydroformylation reactions [7a], as an extension of our previous work on porphyrin encapsulated catalysts [8]. In these non-covalent structures, the Zn(II)salphen units were linked to pyridyl-containing template molecules via Zn(II)–N_{pyr} interactions. Spectroscopic studies revealed a high association constant for this type of supramolecular interaction ($K_{ass} = 10^4$–10^6 M^{-1}). In this contribution, we compare the preferred coordination behavior of substituted salphen ligands in their Zn(II) complexes and illustrate that the intrinsic Lewis acid character of these complexes can be used to build up higher-order systems via either templated or non-templated coordinative patterns that depend on the substitution pattern of the salphen ligand and the donor strength of the axial ligand.

2. Experimental

2.1. Synthesis of 2–4

All materials were commercially purchased and used without further purification. NMR analyses were performed on a Varian (Mercury work station) NMR spectrometer with TMS as an external standard. MS measurements were performed on a Shimadzu LCMS-2010A spectrometer with atmospheric pressure chemical ionization. Complexes **2**–**4** were prepared as reported previously [7a], while mono-imine **1** was prepared according to the literature procedure [9].

2.2. X-ray crystallography of 1 · MeOH, 2 · pyridine, 4 and [1]$_2$ · dabco

X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) at a temperature of 150 K. The structures were solved with automated Patterson methods [10] (compounds **1** · MeOH, (**1**)$_2$ · dabco and **4**) or Direct Methods [11] (for compound **2** · pyridine). The structures were refined with SHELXS-97 [11] against F^2 of all reflections, up to $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1} (compounds **1** · MeOH, **2** · pyridine and **4**) and 0.84 Å^{-1} (for (**1**)$_2$ · dabco). Structure calculations, drawings, and checking for higher symmetry were performed with the PLATON [12] package. Further crystallographic details are given in Tables 1 and 2. Compound **4** crystallizes in the non-centrosymmetric space group *Pc*, but shows a pseudo-center of symmetry (93% fulfilled). The symmetry is broken by the puckering of the salphen ligands with unequal O22–Zn1–O11–C11 and O12–Zn2–O21–C21 torsion angles of 121.9(3)° and −146.4(2)°, respectively. Additionally, a transformation to the centrosymmetric space group $P2_1/c$ is not indicated, because the reflection condition $0k0$: $k = 2n$ is not fulfilled. The structure was refined as a racemic twin with a twin fraction of 0.427(8). The *t*-Bu groups at C125 and C225 were rotationally disordered. Compound (**1**)$_2$ · dabco contained disordered acetonitrile solvent molecules. Their contribution to the structure factors was taken into

Table 1
Crystallographic data for complexes **1** · MeOH and **2** · pyridine

Complex	**1** · MeOH	**2** · pyridine
Formula	$C_{36.6}H_{47.2}Cl_2N_2O_3Zn \cdot CH_3OH$	$C_{30}H_{31}Cl_2N_3O_2Zn$
Formula weight	731.48	601.85
Crystal size (mm)	0.12 × 0.12 × 0.42	0.04 × 0.24 × 0.24
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	6.8779(6)	6.8730(1)
b (Å)	14.438(2)	13.7287(2)
c (Å)	20.834(3)	15.5416(3)
α (°)	107.171(14)	94.1213(6)
β (°)	99.267(11)	97.9518(7)
γ (°)	94.073(9)	102.1837(7)
V (Å^3)	1935.4(5)	1411.89(4)
Z	2	2
D_{calc} (g/cm^3)	1.255	1.416
μ (mm^{-1})	0.811	1.091
Absorption correction range	0.75–0.91	0.90–0.96
Number of collected reflections	53673	27724
Number of unique reflections	8863	6425
Parameters/restraints	425/38	358/0
R_1/wR_2 [$I > 2\sigma(I)$]	0.0495/0.1102	0.0324/0.0754
R_1/wR_2 (all reflections)	0.0827/0.1237	0.0466/0.0822
S	1.022	1.077
Minimum/maximum residual densisty (e/Å^3)	−0.61/0.62	−0.43/0.45

Table 2
Crystallographic data for dimeric complexes **4** and $(\mathbf{1})_2 \cdot$ dabco

Complex	**4**	$(\mathbf{1})_2 \cdot$ dabco
Formula	$C_{56}H_{56}Cl_4N_4O_4Zn_2 \cdot 3(CH_3CN)$	$C_{78}H_{100}Cl_4N_6O_4Zn_2$ + disordered CH_3CN
Formula weight	1244.75	1458.18[a]
Crystal size (mm)	$0.24 \times 0.30 \times 0.48$	$0.30 \times 0.15 \times 0.06$
Crystal system	monoclinic	triclinic
Space group	*Pc* (No. 7)	$P\bar{1}$ (No. 2)
a (Å)	12.3109(1)	13.2536(9)
b (Å)	24.4478(2)	15.7449(14)
c (Å)	11.1669(1)	21.6622(15)
α (°)	90	83.797(6)
β (°)	113.3213(4)	87.319(6)
γ (°)	90	75.383(6)
V (Å^3)	3086.36(5)	4347.6(6)
Z	2	2
D_{calc} (g/cm^3)	1.339	1.114[a]
μ (mm^{-1})	1.001	0.719[a]
Absorption correction range	0.71–0.78	0.59–0.96
Number of collected reflections	49734	90957
Number of unique reflections	13909	15314
Parameters/restraints	786/533	902/48
R_1/wR_2 ($I > 2\sigma(I)$)	0.0274/0.0672	0.0501/0.0970
R_1/wR_2 (all reflections)	0.0306/0.0691	0.0906/0.1062
S	1.045	1.03
Minimum/maximum residual density (e/Å^3)	−0.29/0.27	−0.46/0.41

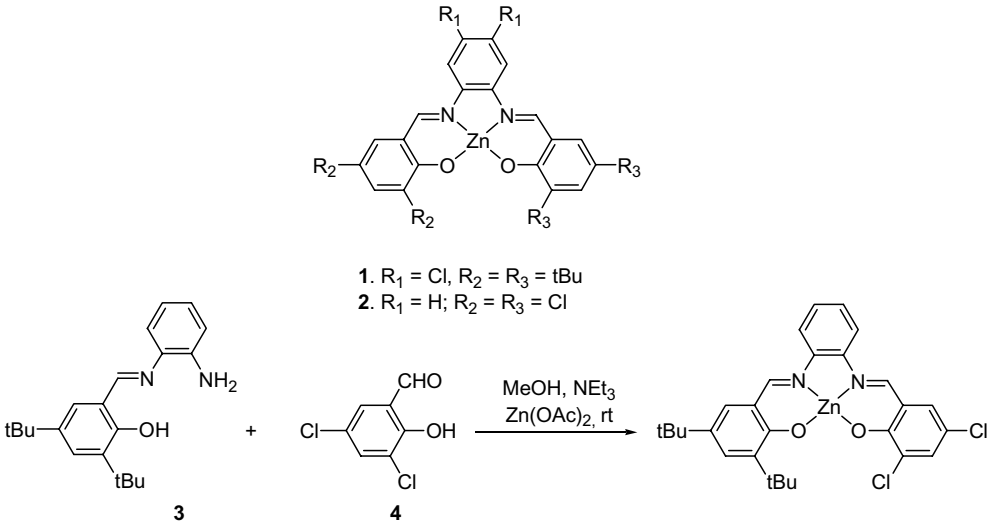
[a] Derived quantities do not contain the contribution of the disordered solvent.

account by back-Fourier transformation using the PLATON/SQUEEZE [12,13] algorithm. The *t*-Bu group at C25 was rotationally disordered.

3. Results and discussion

The Zn(II)salphen complexes **1** and **2** (Scheme 1) were prepared in a one-pot two step procedure using stoichiometric amounts of aldehyde, phenylene diamine and $Zn(OAc)_2 \cdot 2H_2O$ in MeOH at ambient temperature as reported previously [7a]. Compound **3** was prepared using the literature method [9] and was used as starting material for the preparation of **4**. All compounds were isolated as pure powders by a simple filtration step [7a]. The identity of these complexes was established by X-ray crystallography, NMR spectroscopy and MS.

Oxygen donor ligands such as THF and H_2O have recently been reported to coordinate at the axial position in analogous Zn–salphen complexes [3]. This was also demonstrated by the crystallographic analysis of **1** · MeOH/H_2O obtained from a mixture of CH_2Cl_2/MeOH (Fig. 1, Table 1). The bond distances and angles found for **1** correspond to a distorted square pyramidal



Scheme 1. General synthetic approach towards (non)symmetrical Zn(II)salphen complexes.

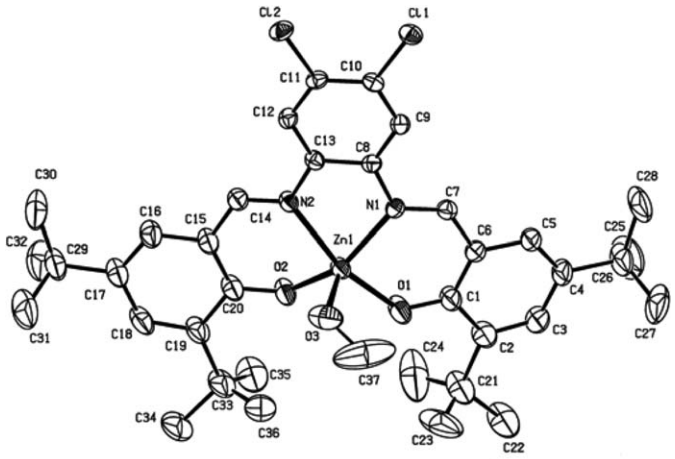


Fig. 1. Displacement ellipsoid plot of the molecular structure of **1** · MeOH/H_2O in the crystal. The axial position is occupied by 60% methanol and 40% water. Hydrogen atoms and non-coordinated methanol solvent molecules have been omitted for clarity and ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°) with su's in parentheses: Zn(1)–O(1) = 1.944(2), Zn(1)–O(2) = 1.973(2), Zn(1)–O(3) = 2.024(3), Zn(1)–N(1) = 2.063(2), Zn(1)–N(2) = 2.109(2); O(1)–Zn(1)–N(2) = 160.31(11), O(2)–Zn(1)–N(1) = 147.42(10), O(1)–Zn(1)–O(3) = 97.86(12), O(2)–Zn(1)–O(3) = 101.90(11), O(3)–Zn(1)–N(1) = 109.22(10), O(3)–Zn(1)–N(2) = 100.82(10).

surrounding of the Zn(II) metal center. The Zn(II) center in **1** · MeOH is tilted from the basal plane as is clear from the observed O–Zn–N angles. This is clearly illustrated by the angles O(1)–Zn(1)–N(2) (160.31(11)°) and O(2)–Zn(1)–N(1) (147.42(10)°) found in **1**. Furthermore, the angles O(1)–Zn(1)–O(3) and O(2)–Zn(1)–O(3) point out that the position of the axial ligand is substantially distorted from ideal geometry. The 3-positioned *t*-Bu groups are a pre-requisite for the existence as a monomeric species both in solution and in the solid state, and without these sterically demanding groups a strong tendency toward dimerization through oxygen-bridging is observed.

It is important to note that complex **2** has less sterically demanding Cl groups present on the 3- and 3′-position of the salphen structure. Complex **2** is only sparingly soluble in the common organic solvents and crystallization from acetonitrile was only successful in the presence of pyridine as co-solvent (ratio 25:1). The molecular structure of **2** · pyridine is depicted in Fig. 2 (see Table 1 for crystallographic details), and pyridine was found as axial ligand bound to the zinc metal, and acetonitrile was present as non-coordinating solvent in the crystal. This clearly demonstrates that pyridine donors are preferred over CH_3CN as axial ligands in these Zn(II)salphen derivatives. The packing diagram of **2** · pyridine (Fig. 2) demonstrates that the axial ligand (pyridine) is located in relatively more accessible voids inside the crystal and consequently no significant steric repulsion is present. The bond distances and angles found for **2** · pyridine correspond to a distorted square pyramidal surrounding of the Zn(II) metal center. The Zn(II) center in **2** · pyridine is somewhat tilted from the basal plane as described by the O–Zn–N angles. Under these crystallization conditions, a monomeric complex was obtained. This is in line with the NMR studies of **2** in the presence of pyridine, but contrasts with earlier reports on similar Zn(II)salphen complexes that were obtained as dimeric species [14].

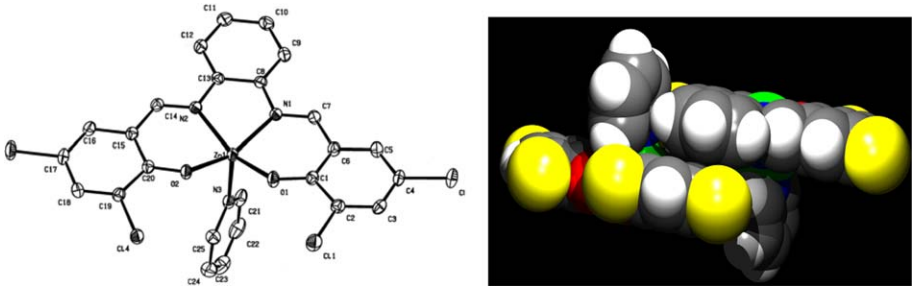


Fig. 2. Displacement ellipsoid plot (left) of the molecular structure of **2** · pyridine in the crystal and a representation of packing (right) showing the face-to-edge interaction between the coordinated pyridine and the adjacent salphen unit. Hydrogen atoms in the left figure and the non-coordinated acetonitrile solvent molecules have been omitted for clarity, and ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°) with su's in parentheses: Zn(1)–O(1) = 1.9944(10), Zn(1)–O(2) = 1.9642(10), Zn(1)–N(1) = 2.0689(12), Zn(1)–N(2) = 2.1131(12), Zn(1)–N(3) = 2.0853(13); N(1)–Zn(1)–N(2) = 78.64(5), O(1)–Zn(1)–O(2) = 93.40(4), N(2)–Zn(1)–N(3) = 104.10(5), O(1)–Zn(1)–N(3) = 99.40(5), O(2)–Zn(1)–N(3) = 97.17(5), N(1)–Zn(1)–N(3) = 106.14(5).

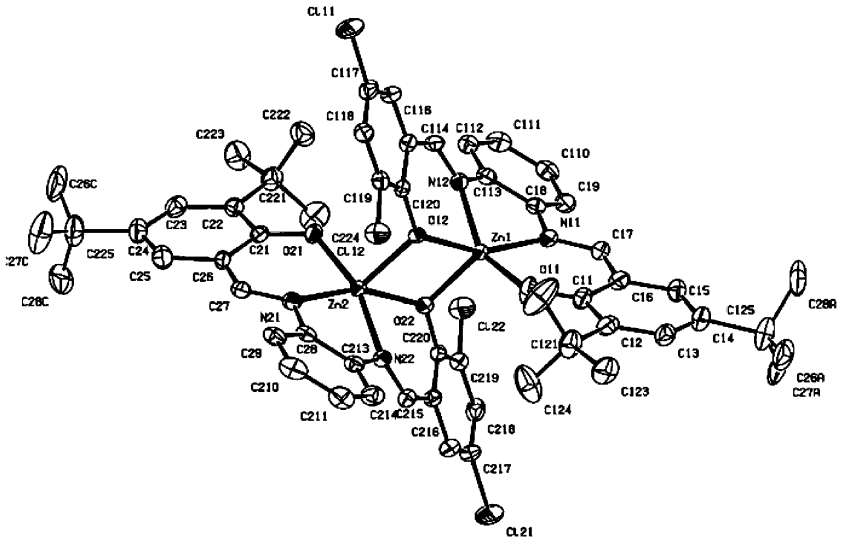
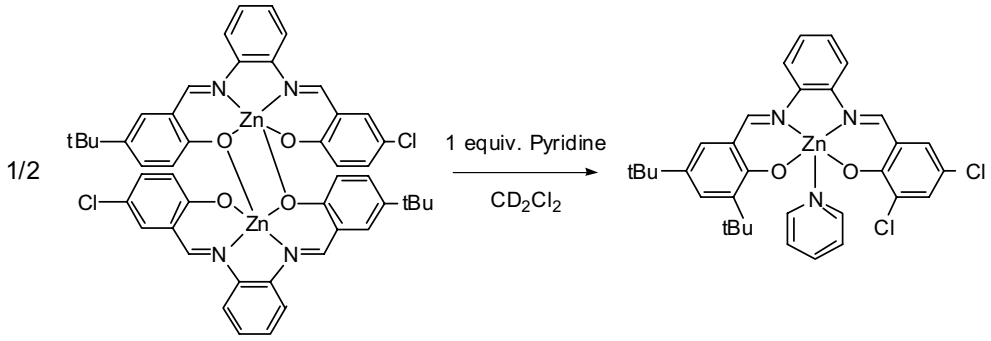


Fig. 3. Displacement ellipsoid plot of the molecular structure of dimeric **4** in the crystal. Hydrogen atoms and the non-coordinated acetonitrile solvent molecules have been omitted for clarity and ellipsoids are shown at the 50% probability level. Only the major conformations of the disordered *t*-Bu groups are shown. Selected bond lengths (Å) and angles (°) with su's in parentheses: Zn(1)–O(11) = 1.930(2), Zn(1)–O(12) = 2.055(2), Zn(1)–O(22) = 2.027(2), Zn(1)–N(11) = 2.080(3), Zn(1)–N(12) = 2.095(3); O(12)–Zn(1)–N(11) = 157.73(10), O(11)–Zn(1)–O(12) = 98.57(9), O(22)–Zn(1)–N(11) = 114.59(10), N(11)–Zn(1)–N(12) = 77.15(11), O(11)–Zn(1)–N(12) = 149.29(11), O(12)–Zn(1)–O(22) = 83.19(8), O(22)–Zn(2)–N(21) = 159.43(10), O(21)–Zn(2)–O(22) = 107.67(9), O(12)–Zn(2)–N(21) = 111.42(10), N(21)–Zn(2)–N(22) = 76.96(11), O(21)–Zn(2)–N(22) = 162.71(10), O(22)–Zn(2)–O(12) = 81.05(8).

Complex **4** was crystallized from acetonitrile and its molecular structure is presented in Fig. 3 (see Table 2 for crystallographic details). Complex **4** forms an interesting dimeric structure [14] in the solid state in which one of the O-atoms of each salphen ligand forms a bridging bond between two zinc centers. The dimer is therefore based on two identical coordination bonds, forming a Zn–O–Zn–O square. The axial oxygen coordination gives rise to a distorted square pyramidal Zn-coordination. The dimer formation causes a profound difference in the Zn–O distances within each monomer unit: Zn(1)–O(11) amounts to 1.930(2) Å, whereas Zn(1)–O(12) is equal to 2.055(2) Å. The two salphen units have an anti-parallel orientation and the *t*-Bu groups of the individual molecules of **4** point away from the adjacent unit in order to minimize steric repulsion. Since the dimer is based on the axial coordination of two oxygen atoms, we reasoned that this structure might be stable in solution. Indeed, a dimeric species was observed by ^{1}H NMR in a non-coordinating solvent (CD_2Cl_2). The resonances for the *t*-Bu groups ($\delta = 1.38$ and 1.27 ppm) and that of the imine protons ($\delta = 8.48$ and 8.25 ppm) appear at different chemical shifts as those of **1**. Interestingly, upon addition of one equivalent of pyridine the pyridyl-H_{ortho} resonance is found at δ 8.37 ppm ($\delta_{free} = 8.57$ ppm, $\Delta\delta = 0.20$ ppm)[1] and the imine protons shift to 8.73 and 8.66 ppm, indicative for the formation of the pyridine complex. In addition, the *t*-Bu groups were now found at lower field at 1.32 and 1.50 ppm, respectively. The changes in the NMR spectra show that **4** is, at least, partly in the dimeric state and an exclusive monomeric complex (**4** · pyridine) is formed upon addition of pyridine (Scheme 2). It is intriguing to note that acetonitrile, the crystallization solvent for **4**, is unable to prevent the dimerization process whereas pyridine readily breaks up the dimeric structure. Further strong evidence of the formation of monomeric, pyridine-ligated **4** was obtained from UV–Vis titration of dimeric **4** with pyridine. The binding curve that was measured in toluene could be fitted to a 1:1 model with an association constant K_{ass} of 4.7×10^5 M^{-1}. Interestingly, this binding is only slightly lower than that found for **1** · pyr ($K_{ass} = 8.0 \times 10^5$ M^{-1}) [7a], which clearly shows that the dimer formation cannot compete with the pyridine coordination. As an extension, we also examined the titration of dimeric **4** with the ditopic, cyclic diamine ligand dabco. Interestingly, the binding curve in toluene was connected with a 2:1 assembly formation with significantly different K_{ass} for the first ($K_1 = 1.9 \times 10^4$ M^{-1}) and second binding ($K_2 = 8.0 \times 10^4$ M^{-1}) of **4** to dabco. This indicates that the binding process of two building blocks of **4** to dabco is cooperative. The stronger binding of the second Zn–salphen unit is likely due to $\pi-\pi$ interactions between two associated salphen-complexes, as also was found previously for porphyrins [15] and is clear from the X-ray structure of (**1**)$_2$ · dabco (vide infra).

This interesting equilibrium between dimeric and monomeric **4** can thus be controlled by axial ligation

[1] The $\Delta\delta$ (0.20 ppm) is fully in line with our previous NMR studies, see [6a].



Scheme 2. Schematic representation of the equilibrium between mono- and dimeric **4**. The 3-positioned Cl/*t*-Bu groups in the dimer have been omitted for clarity.

using sufficiently strong N-donor ligands. The dimer formation of **4** is clearly related to the presence of bulky groups on both the 3 and 3′ positions of the salphen structure. In the absence of these groups and a suitable donor ligand, dimer formation takes place (cf. structure of **4**), while strong donor ligands such as pyridine are able to give rise to monomeric pyridine-ligated complexes (cf., crystal structure of **2** and complex **4** · pyridine, Scheme 2).

We were interested if the observed cooperativity originates from the required dissociation of dimeric **4** and we therefore also studied the assembly formation of monomeric salphen complex **1** with dabco. It was anticipated that **1** in combination with dabco would result in a similar 1:2 assembly, in which the dabco ligand is ditopically bound to two molecules of **1** as found for complex $[\mathbf{4}]_2 \cdot$ dabco (vide supra). First, a **1**/dabco mixture (2:1 ratio) was investigated by ^{1}H NMR (CD_2Cl_2) and a typical upfield shift of the dabco protons was observed ($\Delta\delta = 0.13$ ppm). Furthermore, only a single, sharp resonance pattern was noticed. UV–Vis titration experiments (at 2.7×10^{-5} M for **1**) were carried out in toluene as the solvent to further elaborate on the solution structure. Interestingly, a sigmoidal shaped curve was obtained that is explained by the coincidental small change in extinction coefficient of the bis-dabco-**1** complex compared to free **1**. At increasing concentration of dabco, the 2:1 assembly is in competition with an increasing amount of the 1:1 assembly (i.e., **1** · dabco), giving the titration curve a sigmoidal shape that unfortunately could not be fitted to obtain a reliable association constant. Again, it is clear that the stoichiometry determines the type of assembly formed.

The molecular structure of $(\mathbf{1})_2 \cdot$ dabco in the crystal was solved by X-ray diffraction and is presented in Fig. 4 (see Table 2 for crystallographic details). Some indicative bond distances/angles are listed in the figure's legend. In line with the titration data, both N-atoms of the dabco ligand are coordinating to the Zn(II)-centers of both salphen complexes. The chloride atoms point to the same direction although the salphen building blocks are not completely parallel. The coordination of the dabco N-atoms to Zn(1) and Zn(2) of both molecules of **1** is slightly different, which is expressed by

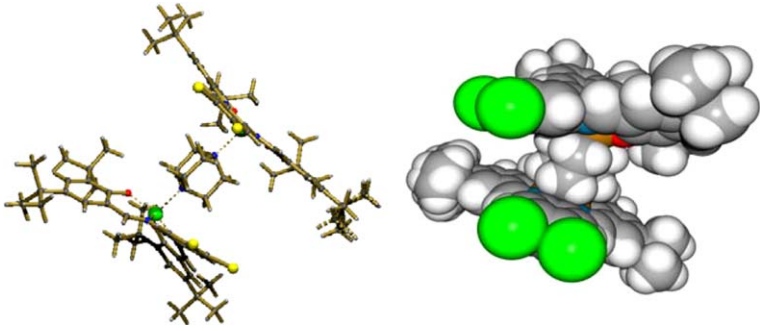


Fig. 4. PLATON generated plots of the molecular structure of the assembly $(\mathbf{1})_2 \cdot$ dabco in the crystal. Hydrogen atoms and co-crystallized solvent molecules have been omitted for clarity. Color codes for the right-hand plot: Cl = green, Zn = brown, N = blue, O = red, C = gray. Selected bond lengths (Å) and angles (°) with su's in parentheses: Zn(1)–O(1) = 1.966(2), Zn(1)–N(1) = 2.109(2), Zn(1)–N(2) = 2.085(2), Zn(1)–N(3) = 2.164(2), Zn(2)–N(4) = 2.128(2); O(1)–Zn(1)–O(2) = 95.87(9), O(3)–Zn(2)–O(4) = 100.11(9), O(1)–Zn(1)–N(3) = 102.59(9), O(3)–Zn(2)–N(4) = 98.20(9), O(2)–Zn(1)–N(3) = 102.18(9), O(4)–Zn(2)–N(4) = 104.67(9). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

small differences in the geometry observed around the Zn(II) centers. This may be related to packing requirements within the crystal lattice.

In summary, we have shown that dimeric Zn(II)salphen structures are accessible through dabco-templated assembly formation. Dimeric Zn(II)salphen structures, connected via axial oxygen coordination of adjacent salphen building blocks, can be reversibly converted into monomeric structures by addition of appropriate Lewis-basic N-donor ligands such as pyridines. Alternatively, dimeric structures can be formed by the application of ditopic ligands such as dabco and the assembly formation can be controlled by the metal-to-ligand ratio. In this way, the distance between two salphen building blocks can be controlled. The combination of these specific Zn(II)salphen–ligand interactions and the use of multi-Zn(II)salphen structures [7a] will enable the preparation of reversible coordination polymers, sensors and devices with potentially interesting photochemical and catalytic features.

Acknowledgments

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Appendix A. Supplementary data

CCDC 273338 (compound **1** · MeOH), 273339 (**2** · pyridine), 273340 (**4**), and 273341 ((**1**)$_2$ · dabco) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.06.069.

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